

HYDROGENATION OF PETROLEUM RESIDUA IN DIFFERENT FLUID MEDIA

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INTRODUCTION

In recent decades, hydroprocessing has played a very important role in upgrading petroleum heavy oils. Compared to thermal processes, hydroprocessing gave distillates not only in higher yield but also in higher quality^{1,2} to meet the environmental constraints on petroleum products. In hydroprocessing, the chemical reactions, such as hydrodesulfurization, hydrogenation, and hydrocracking, occur among the three phases that are gaseous hydrogen, liquid heavy oils and solid catalysts. In order to promote diffusion of hydrogen from gas phase into the surface of catalysts and prolong the catalyst life, high operating pressure is necessary in hydroprocessing. Upgrading petroleum heavy oils in supercritical fluids has been studied in recent years to improve diffusion of reactants and products in reaction systems and to prolong catalyst life. A recent study showed that coke deposits on catalysts were decreased and heteroatom removal was increased when hydrotreating shale oils in supercritical fluids such as toluene and n-heptane³. In such supercritical reaction processes, however, a large amount of supercritical fluid medium (4 times larger than the amount of reactants) has to be used to see the benefits.

Some researchers^{4,5} studied the effects of adding some solvents, for example, on reducing coke formation and increasing heteroatom removal. The solvents used are usually polynuclear aromatics with partial hydrogen saturation. These solvents are considered to facilitate hydrogen transfer by donating or shuttling hydrogen. The conclusions derived from these studies are still controversial. It appears that the effects of the solvents depend strongly on the feedstocks.

In this study, we investigated the effects of adding small concentration of different fluids, e.g., toluene, hexane and pyridine, on catalytic hydrogenation of pyrene and two petroleum distillation residua. Ammonium tetrathiomolybdate was used as a catalyst precursor in the hydrogenation experiments.

EXPERIMENTAL

Pyrene (99% purity) was supplied by Aldrich Chemical Company Inc. The properties of the petroleum residua used in the present work, an atmospheric residue (AR) and a vacuum residue (VR), are listed in Table 1. Hydrogen gas used in the experiments was ultra high purity hydrogen supplied by MG Industries. Ammonium tetrathiomolybdate (ATTM) supplied by Aldrich Chemical Company Inc. was used as a catalyst precursor. Its purity is 99.97%. ATTM decomposes to amorphous MoS₂, H₂S and NH₃ when heated in hydrogen. MoS₂ has catalytic activity for pyrene and petroleum residua hydrogenation.

Table 1. Properties of petroleum residua

	Asphaltene content wt %	H/C atomic ratio	Sulfur content wt %	Residue fraction (525 °C+) / wt %
AR	9.2	1.58	3.9	55.7
VR	14.0	1.33	4.8	88.2

The n-hexane, toluene, pyridine and water were used in the present work to investigate the effect of the fluid media on the pyrene and petroleum residua hydrogenation. The n-hexane and toluene were supplied by J. T. Baker Inc. The purity was more than 95 and 99.9 % for n-hexane and toluene, respectively. Deionized water with high purity was used in the experiments.

Reactions were carried out in 316 stainless steel batch reactors (20 mL) heated in a fluidized-sand bath. Except for investigating the effect of the amount of the fluid media, the quantity of the media used in the experiments was kept a constant at 2 mol % with respect to the quantity of hydrogen initially present. For instance, approximately 0.16 g of toluene was added per 0.083 mol hydrogen. ATTM of 3.8 wt% based on reactant (pyrene or petroleum residue) was added into the reactor in each run, which corresponds to a metal loading of 1.5 wt %. After adding the reactant (pyrene, AR

or VR), ATTM catalyst precursor and liquid fluid medium, the headspace gas in the reactor was replaced three times with hydrogen before the reactor was charged with hydrogen to the desired cold pressure. Then, the reactor was plunged into a preheated sand bath. The reactor contents reached the desired reaction temperature within 3 minutes. At the end of the reaction, the reactor was quenched in cold water. Products and catalyst mixtures were washed with toluene. Then the catalyst was separated from the toluene solution by filtration. After evaporation in Rotavapor, the toluene solvent and the fluid medium were separated and the product mixture was recovered.

Products resulted from pyrene hydrogenation were characterized by GC-MS using standard compounds, and measured quantitatively by GC-FID with a DB-17 capillary column. Products from residue hydrogenation were analyzed by CHN-600 elemental analyzer and LECO sulfur analyzer to determinate H/C atomic ratio and sulfur content of the product mixture. Asphaltene (here defined as materials insoluble in n-hexane) contents of the products were measured by treating the sample (0.2 ± 0.02 g) with n-hexane (20 mL) in an ultrasonic water bath for 5 minutes, followed by setting for another 10 minutes before vacuum filtration through a previously weighed GF/A filter paper. The filtration residue was washed with excess n-hexane (about 30 mL). The solid residue and the sample vial (as some residue remains adhered to the vial wall) were dried in a vacuum oven and then weighed to determine the asphaltene content of the sample.

RESULTS AND DISCUSSION

Pyrene hydrogenation. Products of pyrene hydrogenation were mainly composed of dihydropyrene, tetrahydropyrene and hexahydropyrene. At high pyrene conversion, some amount of decahydropyrene was also found in the product mixture. Pyrene conversion was defined as the difference of pyrene content in reactant and product mixture in percent. Figure 1 compares pyrene conversion obtained in four binary mixtures of hydrogen with n-hexane, toluene, pyridine, and water (containing 2 mol % of each compound in the starting mixtures with respect to the hydrogen) to that obtained in pure hydrogen at 375 °C and 90 min. The cold hydrogen pressure in the reactor determines the hydrogen mole content in the reactant mixture, and changes the initial total pressure at the reaction temperature, as shown in Table 2. A pyrene conversion 23 % was obtained at 0.083 mol hydrogen in pure H₂ gas, reaching the thermodynamic equilibrium. It is notable that a much higher conversion was obtained with the addition of the second compound at the same hydrogen mole content, except in the case of adding pyridine at a relatively high pressure. The highest conversion (64%) was obtained with the addition of toluene, followed by the addition of water (61%) and n-hexane (56%). Although it is not clear why conversion decreases from 42% to 24% there were signs of pyridine hydrogenation at 1750 psi when the total pressure was increased from 1400 to 1750 psi in pyridine + hydrogen mixtures. It is clearly shown in Figure 1 that the addition of toluene, n-hexane or water strongly promoted the pyrene hydrogenation at the same partial pressure of H₂ initially.

Table 2. Changes of cold hydrogen pressure and corresponding hydrogen molar content and initial total reactor pressure at 375 °C

H ₂ mole	H ₂ cold Pressure /psi	Initial reactor pressure / psi			
		H ₂	H ₂ +n-hexane	H ₂ +toluene	H ₂ +pyridine
0.017	200	400	350	430	350
0.034	400	800	700	810	780
0.052	600	1200	1100	1060	1150
0.069	800	1700	1460	1520	1400
0.083	1000	2000	1919	1850	1750

The effect of increasing the toluene concentration in the binary mixture on pyrene conversion is shown in Figure 2. A significant increase in the conversion was observed upon adding a small amount of toluene and the conversion quickly leveled off with further addition of toluene. Toluene, as a mono-ring aromatic compound, does not act as a hydrogen shuttle, like some polynuclear aromatics that transfer radical hydrogen to hydrogen acceptors⁷. The trend in Figure 2 clearly shows that a step increase was obtained in pyrene conversion upon incremental addition of toluene, related most likely to large changes in critical properties of the H₂ and toluene mixture compared to those of H₂ alone. Further increase in toluene concentration may not cause much change in the critical properties of the mixture.

Residua hydrogenation. The change in the n-hexane insoluble components (HI, asphaltenes) content of the residua samples was used as a preliminary measure for the extent of hydrogenation. Figure 3-4 shows the change in HI of AR and VR residua as a function of hydrogen mole content in pure hydrogen and three binary mixtures. The reaction conditions were the same as those of pyrene hydrogenation. For the mixture of hydrogen with toluene, water, and pyridine, the concentration of the second fluid was kept constant at 2 mole % of the initial hydrogen. The trends

are remarkably similar to those obtained with pyrene hydrogenation in the same fluid mixtures. The H_2 + toluene mixtures produced the highest conversion and all binary mixtures gave higher conversions than that achieved with hydrogen alone. The trends of asphaltene reduction in the mixtures of H_2 + water were similar to those with H_2 + toluene mixtures and also gave higher reductions in asphaltenes than those obtained by pure hydrogen. Comparing Figure 3 with 4, under the present reaction conditions, it is clearly shown that the asphaltene reduction by hydrogenation depends strongly on the addition of the second compound for both residua, AR and VR.

Table 3 shows for both residua the H/C atomic ratio and sulfur content of the products obtained by hydrogenation of AR and VR in pure hydrogen, and in mixtures of H_2 + toluene. There was not much change in the elemental composition under the present reaction conditions, and only slight increases were observed in the H/C ratios of the hydrogenated products in the case of H_2 + toluene. The reductions in sulfur contents were small, and showed, in general, that ATTM has little desulfurization activity under the reaction conditions.

Table 3. Comparison of H/C ratio and sulfur content in hydrogenated products

Feedstock	Fluid media	H/C atomic ratio	Sulfur content wt %
AR	H_2	1.58	3.61
	H_2 + Toluene	1.60	3.62
VR	H_2	1.33	4.73
	H_2 + Toluene	1.37	4.60

CONCLUSIONS

The addition of a small amount of fluids (toluene, water or n-hexane) strongly promotes the hydrogenation of pyrene with ATTM. In hydrogenation of petroleum residua, the addition of the fluids reduced the asphaltene content of the products and increased the H/C ratio of hydrogenated products. These promotional effects could result from the changes in the supercritical properties of the fluid media (mixture of hydrogen and the added second compound).

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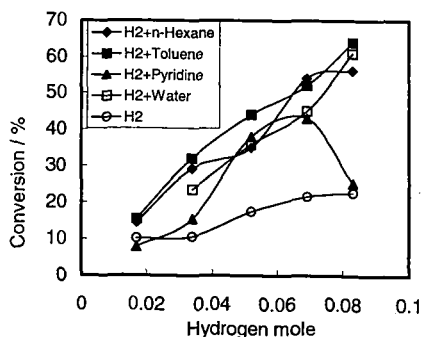


Figure 1. Pyrene hydrogenation in different fluid media. 375 °C, 90 min.

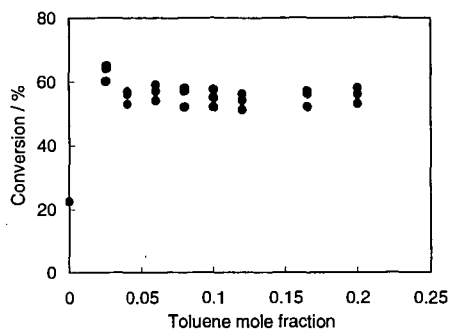


Figure 2. Pyrene conversion as a function of toluene mole fraction in mixtures of H_2 -Toluene ($H_2 = 0.063$ mole). 375 °C, 1000 psi H_2 (cold), 90 min.

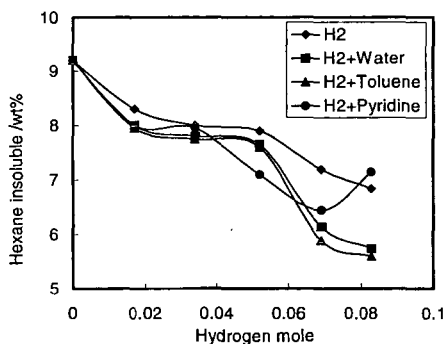


Figure 3. Asphaltene content in products from hydrogenation of AR in different fluid media. 375 °C, 1000 psi H_2 (cold), 90 min.

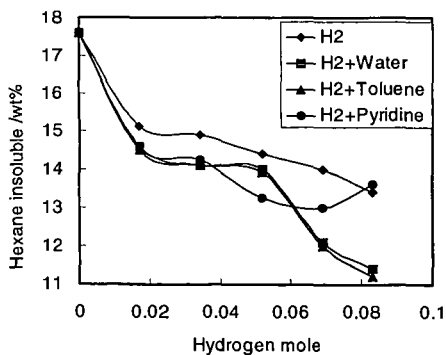


Figure 4. Asphaltene content in products from hydrogenation of VR in different fluid media. 375 °C, 1000 psi H_2 (cold), 90 min.